

STUDIES OF THE SMALLER BORON HYDRIDES AND THEIR DERIVATIVES

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Abstract - A survey of systematic studies of the smaller boron hydrides is presented. Relative Brønsted acidities have been determined and the Lewis base properties of anions derived by removing a bridge proton have been investigated. Addition of BH_3 to these anions results in expanded borane anion structures. These expanded structures can be converted on a large scale to B_5H_{11} , B_6H_{10} , and B_6H_{12} in high yield. Principles are described for preparing certain specifically methyl substituted derivatives of the smaller boron hydrides and boron hydride anions. The nature of the basic boron-boron site in B_6H_{10} and in boron hydride anions is discussed with respect to fluxional properties and the formation of selected metallo-boranes. The structures and properties of some bis-ligand adducts of B_5H_9 and B_6H_{10} ($\text{B}_5\text{H}_9\text{L}_2$ and $\text{B}_6\text{H}_{10}\text{L}_2$) and their relationships to the hypho class of cluster systems is discussed.

INTRODUCTION

The apparently unique structures, bonding, and chemistry of the boron hydrides have served as a stimulus for a relatively small number of inorganic chemists who have concerned themselves with this class of compounds. Their efforts have contributed a wide variety of new chemistry ranging from the hydroboration process through the preparation of polyhedral borane anions and related carboranes and metalloboranes. The novelty of this chemistry is easily recognized. But more important is the underlying relationship of these materials and their properties to other areas of chemistry. Thus the fluxional properties of molecules, metal cluster compounds, and transition metal hydrides are areas to which boron hydrides relate significantly.

While the stage has been set for understanding much new chemistry, there still remain relatively unexamined boron hydride systems which have the potential for providing new insights. Only two boron hydrides, B_2H_6 and $\text{B}_{10}\text{H}_{14}$, have been studied extensively. Intermediate boron hydrides have received significantly less attention. This disparity arises from the fact that with the exception of B_5H_9 , the intermediate boron hydrides, until relatively recently, had been either unavailable or practical syntheses on the basis of product yield were unknown.

Since 1967 the research group of the author has been mainly concerned with the intermediate boron hydrides. Among our contributions has been the development of good yield, potentially large scale syntheses of B_6H_{10} , B_6H_{12} , and B_5H_{11} . These syntheses and the principles behind them hold the key to future interest and uses of the intermediate boron hydrides. This paper is concerned with a brief survey of the chemical and structural relationships among some of the smaller boron hydrides and their derivatives. Particular emphasis is placed upon results obtained from the author's laboratory in the period of 1967-1976.

DEPROTONATION AND POLYHEDRAL EXPANSION OF BORON HYDRIDE SYSTEMS

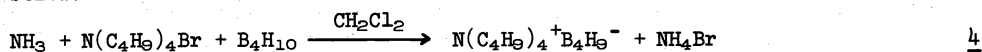
A commonly recognized property of the boron hydrides is the apparent negative (hydridic) character of their hydrogens. Protolysis reactions yield hydrogen gas. That certain hydrogens in boron hydrides can function as though they are protonic in nature was first demonstrated in 1956 when $\text{B}_{10}\text{H}_{14}$ was shown to function as a monoprotic Brønsted acid with the proton source being the B-H-B bridge system (1). It was not until 1967, however, that definitive evidence for the Brønsted acidity of a lower boron hydride, B_5H_9 , was offered (2). Onak, Dunks, Searcy, and Speilman (2a); Gaines and Iorns (2b); Geanangel and Shore (2c) independently deprotonated B_5H_9 to obtain the B_5H_8^- ion. Since that time, additional deprotonation studies in this laboratory have shown that many of the lower and intermediate boron hydrides and their alkyl and halo derivatives can function as monoprotic Brønsted

acids with a bridging hydrogen serving as the proton source (3). Bases such as ammonia (3a, 3e, 3f, 4), lithium alkyls (2b, 2c, 5), and metal hydrides (2a, 2c, 3a, 3f) have been employed. Some examples of deprotonation reactions observed in this laboratory are shown below.



The hydrides represented in the above reactions are of particular interest to the present discussion. It should be recognized, however, that other boron hydrides smaller than $\text{B}_{10}\text{H}_{14}$: B_5H_{11} (3a), B_6H_{12} (3a), and B_9H_{15} (6) have been deprotonated also. However, $\text{B}_5\text{H}_{10}^-$ is not yet well-characterized and the anions $\text{B}_6\text{H}_{11}^-$ and $\text{B}_9\text{H}_{14}^-$ are more readily accessible through other routes.

Convenient, large scale syntheses of salts of the anions shown above have been developed (3). Deprotonation reactions using ammonia as the deprotonating agent have been developed into simple procedures for preparing tetraalkylammonium salts (3e). An example preparation is given below.

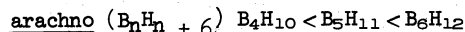
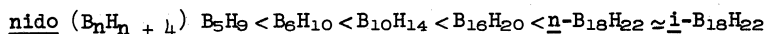


Quaternary ammonium and quaternary phosphonium salts of the anions show minimal decomposition over a period of several hours at room temperature and are conveniently handled (3a,c).

From proton competition reactions such as the following example, the relative Brønsted acidities of several boron hydrides have been established (3a).



These results supplemented by observations from other laboratories (7) indicate the following orderings of the Brønsted acidities of the nido and arachno boron hydrides.



Within each class of hydrides, the acidity increases with increasing size of the boron framework. These results support a prediction made in 1959 by Parry and Edwards (8) which assumed that acidity of bridge hydrogens could be related to the extent of electron delocalization in the boron framework. The arachno hydrides are more acidic in general than the nido hydrides: $\text{B}_4\text{H}_{10} > \text{B}_6\text{H}_{10}$.

Effects of substituents on Brønsted acidity have also been noted. An alkyl substituted B_5H_9 or B_6H_{10} is less acidic than the parent hydride while a halo substituted (Cl or Br), substituted molecule is more acidic than the parent B_5H_9 (3b) or B_6H_{10} (9).

The structures of the boron hydrides and their conjugate bases from reactions 1-3 are shown in Fig. 1 below. The structures presented for the anions are based upon nmr spectroscopic (3a, 3b, 3g) and X-ray studies (10, 11) of the anions or derivatives of the anions. These structures are limiting or static structures since the anions are fluxional on the proton and boron-11 nmr time scales.

For the pyramidal ions B_5H_8^- and B_6H_9^- this fluxionality seems to involve migration of bridging hydrogens while terminal hydrogens are apparently static (3b, 3c, 3g). Potassium salts of B_5H_8^- and B_6H_9^- in $(\text{CH}_3)_2\text{O}$ are not quenched at temperatures as low as -135° (12). A possible mechanism for such hydrogen migration in these ions is presented in Fig. 2 below (3g). The B_6H_{10} molecule is also fluxional with respect to bridge hydrogen migration (13) and the same mechanism can be considered to be operative for B_6H_{10} as well.

In the case of the B_4H_9^- ion, the nmr spectra reveal distinct stages of fluxionality (3a). Figure 3 presents boron-11 nmr spectra of this ion at several temperatures. At -90° multiplicities and peak areas point to an unambiguous assignment of a static structure. On warming the sample, the triplet assigned to B_2 and B_4 becomes a singlet, but does not shift position. On the other hand, warming causes the triplet assigned to B_1 and the doublet assigned to B_3 to first collapse to singlets and upon further warming disappear while a doublet appears at a position which is equal to the average of the chemical shifts of B_1 and B_3 . At this stage, -20° , the axial hydrogen on B_1 and the axial hydrogen on B_3 appear to be static compared to rapid migration of the remaining hydrogen atoms. At about 40°

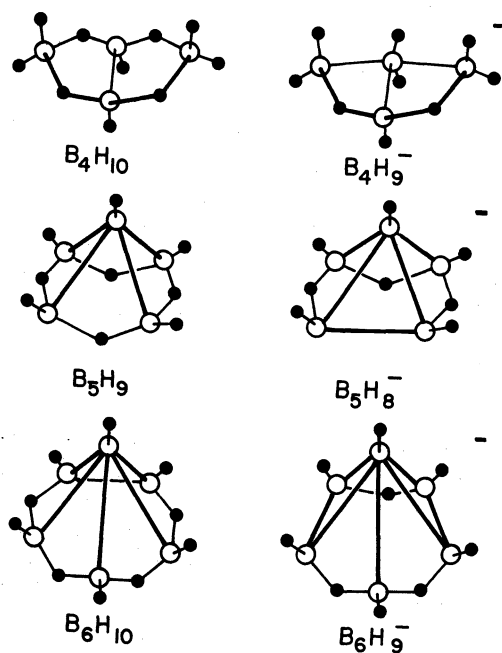


Fig. 1. Conjugate acid-base pairs.

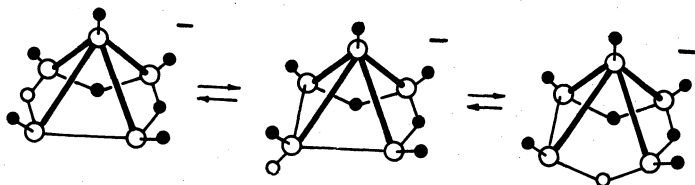


Fig. 2. Possible mechanism for hydrogen bridge migration.

there is no longer any apparent spin-spin coupling between boron and hydrogen. All of the hydrogens appear to be fluxional. The proton nmr spectrum at this temperature is a single resonance which is in accord with this premise.

Removal of a bridging proton from a boron hydride creates a boron-boron bond which is susceptible to insertion of an electrophilic reagent. By inserting BH_3 into this site a series of previously unknown boron hydride anions was generated (3a). The structures of these anions are depicted in Fig. 4 below. NMR spectroscopy, proton and boron-11, was used to

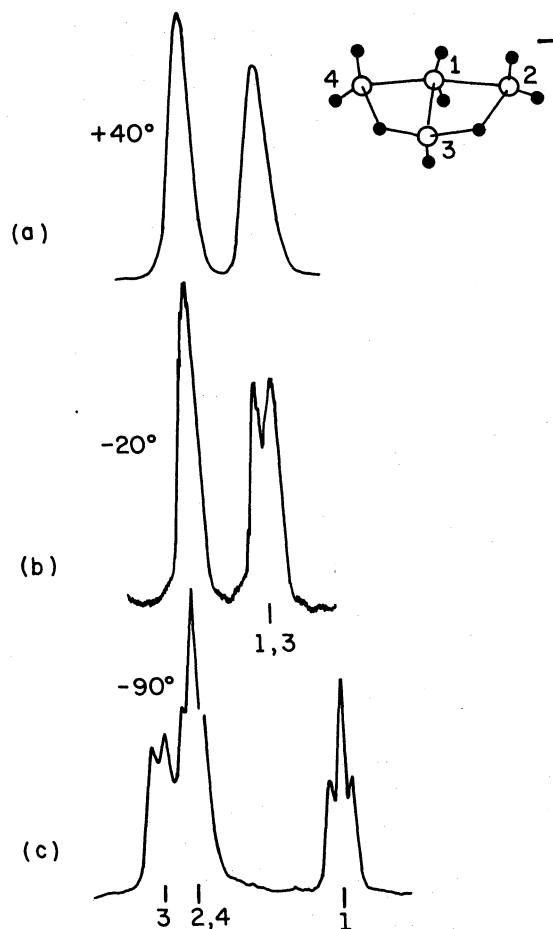
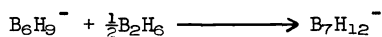
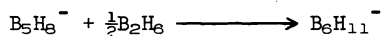


Fig. 3. The 32.1 MHz boron-11 NMR spectrum of $B_4H_9^-$: (a) $[(C_6H_5)_3FCD_3][B_4H_9^-]$ in CD_2Cl_2 at $+40^\circ$, (b) $[(C_6H_5)_3FCD_3][B_4H_9^-]$ in CD_2Cl_2 at -20° , (c) $NH_4^+B_4H_9^-$ in $(CH_3)_2O$ at -90° .



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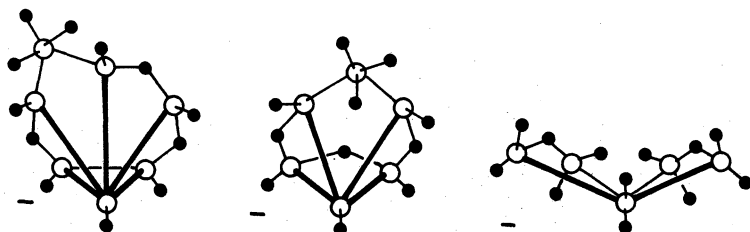


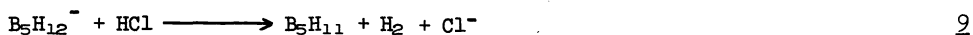
Fig. 4. Structures: $B_5H_{12}^-$, $B_6H_{11}^-$, $B_7H_{12}^-$

infer the structures of $B_5H_{12}^-$ and $B_6H_{11}^-$ (3a). The structure of $B_7H_{12}^-$ is inferred from the X-ray structure of the derivative $Fe(CO)_4-B_7H_{12}^-$ (14). The $B_6H_{11}^-$ and $B_7H_{12}^-$ ions are pyramidal structures with a BH_3 group inserted into a basal bridging position. These ions are fluxional with BH_3 hydrogens exchanging with basal bridging hydrogens. The low temperature proton nmr spectrum of $B_6H_{11}^-$ suggests a static structure in which one of the BH_3 hydrogens has a resonance which is suggestive of a bridging hydrogen. By the same token the X-ray structure of the $B_7H_{12}^-$ derivative, $Fe(CO)_4-B_7H_{12}^-$ indicates a unique BH_3 hydrogen which is in a 'pseudo' bridging position.

From boron-11 and proton nmr spectra of $[P(CD_3)(C_6H_5)_3]^+[B_5H_{12}^-]$ in a $CD_2Cl_2-CHClF_2$ mixture the $B_5H_{12}^-$ ion is considered to be a four-sided pyramid in which all of the hydrogens are fluxional down to at least -90° (3a). This is the only example of a pyramidal boron hydride species in which all of the hydrogens are involved in the fluxional process. From the proton nmr spectrum at -135° (3a) a possible static structure was derived.

GOOD YIELD SYNTHESSES OF BORON HYDRIDES

Treatment of $B_5H_{12}^-$ and $B_6H_{11}^-$ with HCl leads to the preparation of B_5H_{11} and B_6H_{12} in yields of at least 60% (3a).

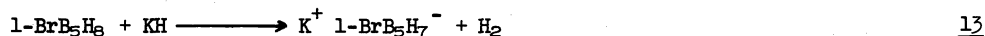


Treatment of $B_6H_{11}^-$ with B_2H_6 results in the formation of B_8H_{10} in yields up to 30% (15).



These syntheses represent significant advancements in the preparative chemistry of the smaller boron hydrides. Earlier methods for the preparation of B_6H_{10} and B_6H_{12} in particular gave small yields of products and required relatively laborious procedures (16).

An improved synthetic procedure which is superior to reaction 11 above has also been developed in our laboratories (17). The yield of B_6H_{10} is approximately doubled (60-75%) and isolation of the product is more easily and rapidly accomplished. The entire process is represented by the following reactions.



The basic principle involved in the preparative procedures described above is polyhedral expansion through removal of a bridge proton followed by insertion of a BH_3 group into the boron-boron bond and then conversion of the resulting anion to a neutral boron hydride containing one more boron than the starting material. These procedures have been extended to the preparation of derivatives of the boron hydrides.

Starting with 1-Br-2- $CH_3B_5H_7$ the compound 2- $CH_3B_6H_9$ has been prepared in 55% yield through a sequence of reactions analogous to 12-14 (17). The compound 2- BrB_6H_9 has been conveniently prepared in 60% yield from the reaction of B_6H_{10} with BBr_3 (18). Like the parent B_6H_{10} molecule, 2- $CH_3B_6H_9$ and 2- BrB_6H_9 contain fluxional bridge hydrogens. Low temperature proton nmr spectra of these compounds reveal that the static molecular structures are asymmetric due to the position of the basal boron-boron bond in each molecule (13). See Fig. 5. This pair of compounds suggests that the terminal substituents produce opposite

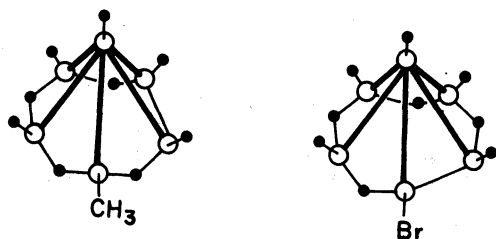


Fig. 5. Molecular structures: 2- $CH_3B_6H_9$ and 2- BrB_6H_9 .

inductive effects which determine the position of the boron-boron bond in each quenched molecular structure.

Starting with 1-CH₃B₅H₉ and employing a sequence reactions analogous to those which give B₆H₁₂ (3a), the compound 3-CH₃B₆H₁₁ has been prepared in 80% yield (19). The preparation is specific with respect to the position of the methyl group in the product.

Using 3-CH₃B₆H₁₁ as the starting point a sequence of steps has been developed to progressively degrade the B₆ framework to yield smaller, specifically methyl substituted boranes (19). The basic principle involves cleavage of the boron framework by ammonia to give an ionic product containing a methyl substituted anion which is then converted to a neutral borane by a protonation reaction. Fig. 6 gives the sequential degradation and protonation reactions which have been employed.

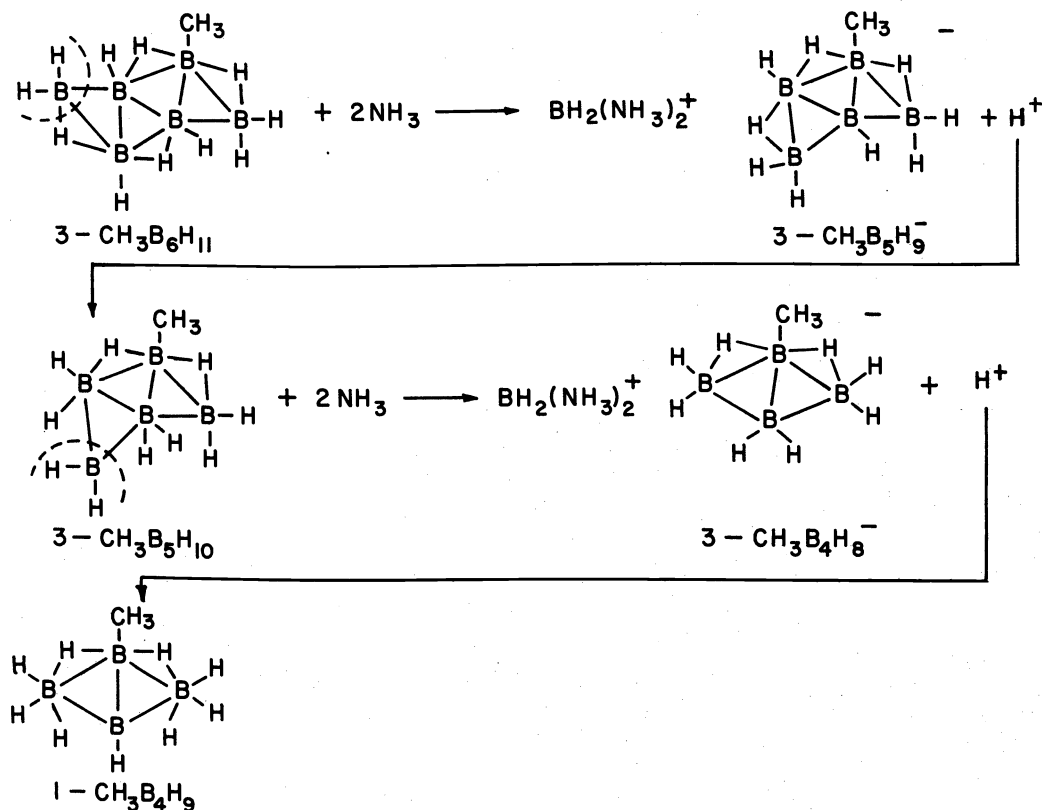


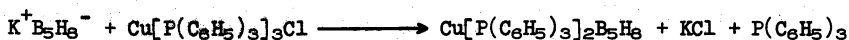
Fig. 6. Schematic representations of smaller organoborane syntheses (Topological structures not necessarily indicating chemical bonds are employed.)

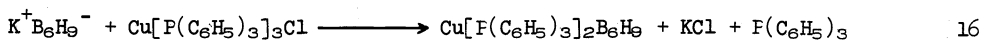
The reactions shown above give good yield synthetic procedures for previously unknown organoboranes. These reactions also indicate 2 points of additional interest: 1) There is a directive effect in each cleavage reaction. A boron atom farthest from the methyl group is split-off from the framework. 2) In each cleavage reaction the remaining anion framework retains its structural integrity and is related to the framework of the boron hydride from which it is derived.

METALLOBORANES

Copper Derivatives

The anions B₅H₈⁻ and B₆H₉⁻ have proved to be susceptible to insertion of a variety of electrophilic reagents in addition to the BH₃ insertion described above. Gaines and co-workers, for example, have successfully inserted Group IV elements into the boron-boron bond (20). In this laboratory we have inserted a number of metals. Through the following reactions Cu(I) was inserted into a bridging site in B₅H₈⁻ and B₆H₉⁻ (21).





As the isolated solids, $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_5\text{H}_9$ and $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_6\text{H}_9$ are air stable for extended periods of time (the order of days) at room temperature.

Unlike the previously reported Cu(I)-borane derivatives: $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{BH}_4$ (22a), $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_3\text{H}_8$ (22b), and $[\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2]_2\text{B}_{10}\text{H}_{10}$ (22c), there is no apparent Cu-H-B interaction in $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_5\text{H}_9$ (21,23). Thus, for example, $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_3\text{H}_8$ is represented by a valence structure (Fig. 7) in which the principal mode of bonding of Cu(II) to the B_3H_8^- moiety is represented by Cu-H-B bonds. On the other hand in the case of

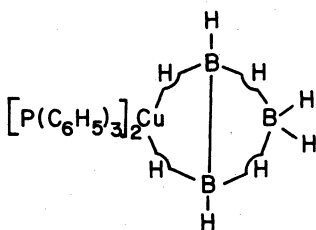


Fig. 7. The principal valence structure of $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_3\text{H}_8$.

$\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_3\text{H}_8$, infrared (23) and nmr (21a) spectra favor a structure in which trigonal Cu(I) is bonded to the basal B-B bond of the B_3H_8^- unit through a 3-center B-Cu-B bond. Figure 8 gives a representation of the molecular structure and valence structure of this molecule based upon its nmr (21a) and infrared spectra. A further point of interest is that the proton nmr spectra reveal that the molecule is nonfluxional even at 24°C in CH_2Cl_2 . The molecular structure of $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_5\text{H}_9$ has been recently determined by Greenwood and

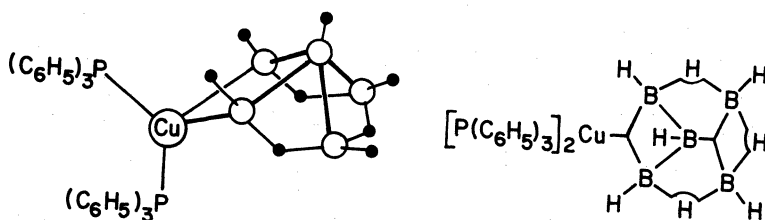


Fig. 8. The molecular structure and principal valence structure of $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_5\text{H}_9$.

co-workers (24) in an X-ray study. Their results support the independent conclusions drawn earlier from nmr (21a) and infrared spectra (23).

The structure of $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_6\text{H}_9$ is probably that shown in Fig. 9. This structure with the metal inserted into a site which is non-adjacent to the remaining basal B-B bond in the B_6H_9 unit is favored in view of the precedent established by the structure of $(\text{THF})_2\text{Mg}(\text{B}_6\text{H}_9)_2$ (11) and inferred by the structure of $\text{Fe}(\text{CO})_4\text{-B}_7\text{H}_{12}^-$ (14).

The compound $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_6\text{H}_9$ is stereochemically nonrigid. Proton nmr in CH_2Cl_2 at 25°C are consistent with both the $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ group and the bridge hydrogens being involved in migration among the available sites for bridge bonding. At -90° the $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ group is effectively rigid but the bridging hydrogens are still in motion (21c).

Recently K. Inkrott of this laboratory prepared $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_4\text{H}_9$ by two routes:

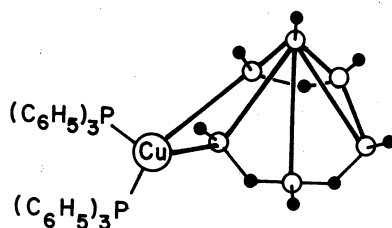
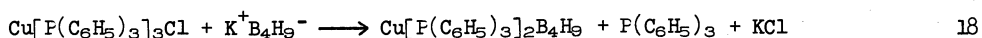
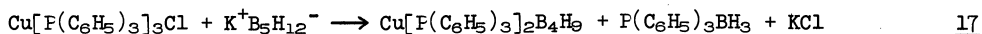


Fig. 9. Proposed structure of $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_6\text{H}_9$



As the isolated solid, $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{B}_4\text{H}_9$ is stable at room temperature for several days. Preliminary nmr spectra suggest that this molecule is a four sided pyramid with a BH_2 group at the apex. The available evidence is not inconsistent with a $\text{Cu}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ occupying a basal vertex site.

IRON DERIVATIVES

The basal B-B bond in B_6H_{10} is susceptible to insertion of electrophilic reagents. We have protonated B_6H_{10} to form $\text{B}_6\text{H}_{11}^+$ and have isolated the salts $\text{B}_6\text{H}_{11}^+\text{BCl}_4^-$ and $2\text{-CH}_3\text{B}_6\text{H}_{10}^+\text{BCl}_4^-$



(25). The $\text{B}_6\text{H}_{11}^+$ cation is the only known example of a polyhedral borane cation (Fig. 10).

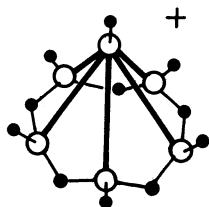
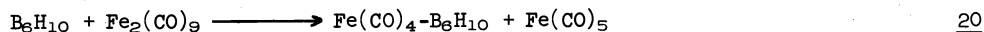


Fig. 10. The structure of $\text{B}_6\text{H}_{11}^+$.

Several transition metals (Fe, Pt, Rh) have been added to the basal B-B bond of B_6H_{10} (26). Davison, Traficante, and Wreford (26a, 26b) have observed the following reaction.



Our objective has been to use compounds such as $\text{Fe}(\text{CO})_4\text{B}_6\text{H}_{10}$ as building blocks to higher metalloboranes through a sequence of steps much like our rational syntheses of boron hydrides described earlier in this article.

Deprotonation of $\text{Fe}(\text{CO})_4\text{-B}_6\text{H}_{10}$ is readily achieved. This compound is, in fact, a stronger



Brønsted acid than B_6H_{10} (14a). The ion $\text{Fe}(\text{CO})_4\text{-B}_6\text{H}_9^-$ is stereochemically nonrigid on the boron-11 and proton nmr time scales. J. Ragaini of this laboratory found that in THF-d_8 at room temperature the $\text{Fe}(\text{CO})_4$ group and the bridging hydrogens move among the available bridging sites. At -50° the $\text{Fe}(\text{CO})_4$ group is apparently rigid while the bridging protons

are still fluxional. Around -100° the bridging protons become apparently fixed. The static structure is asymmetric (Fig. 11).

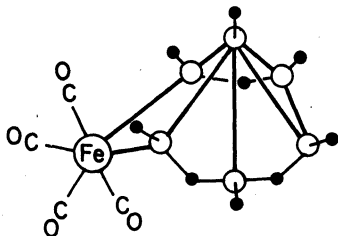


Fig. 11. The structure of $\text{Fe}(\text{CO})_4\text{-B}_6\text{H}_6^-$.

Addition of B_2H_6 to $\text{Fe}(\text{CO})_4\text{-B}_6\text{H}_6^-$ yields $\text{Fe}(\text{CO})_4\text{-B}_7\text{H}_{12}^-$ (14). The salt $\text{N}(\underline{n}\text{-C}_4\text{H}_9)_4^+ \text{Fe}(\text{CO})_4\text{-Fe}(\text{CO})_4\text{-B}_6\text{H}_6^- + \frac{1}{2}\text{B}_2\text{H}_6 \longrightarrow \text{Fe}(\text{CO})_4\text{-B}_7\text{H}_{12}^-$ 22

$\text{B}_7\text{H}_{12}^-$ has been isolated and the structure has been determined from an X-ray study (14). Two views of the structure of the $\text{Fe}(\text{CO})_4\text{-B}_7\text{H}_{12}^-$ ion are shown in Fig. 12. The structure can be considered to be a B_6H_6^- pentagonal pyramid into which an $\text{Fe}(\text{CO})_4$ group and a BH_3 group have been inserted into non-adjacent bridging sites. Structural parameters are consistent with

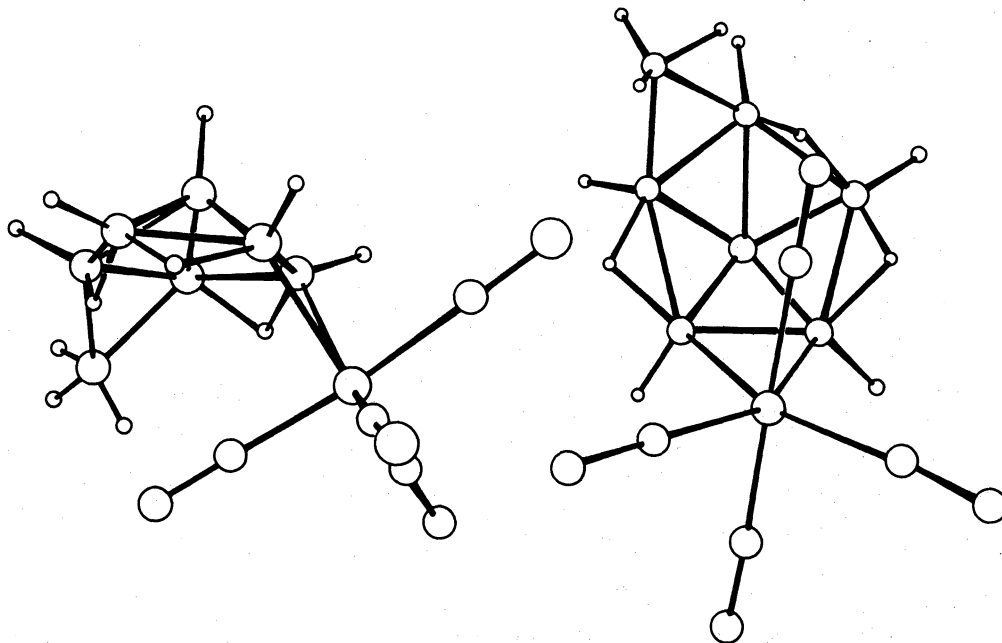
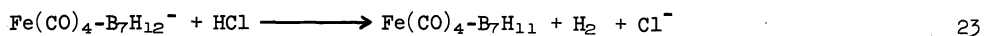


Fig. 12. Two views of the structure of $\text{Fe}(\text{CO})_4\text{-B}_7\text{H}_{12}^-$.

the existence of a B-Fe-B β -center bond, the iron being formally dsp^3 hybridized.

Treatment of $Fe(CO)_4-B_7H_{12}^-$ with HCl yields the following reaction (14a). The product



$Fe(CO)_4-B_7H_{11}$ has been identified by its mass spectrum. It decomposes to yield $Fe(CO)_4-B_6H_{10}$ and has not yet been isolated in the pure state. However, the impure product is stable at room temperature in the air for short periods of time. It is noteworthy that the boron hydride B_7H_{11} has never been isolated although it has been tentatively identified by means of mass spectrometry (14a). It seems likely that the presence of the $Fe(CO)_4$ group in a bridging site has a stabilizing effect as in the case of the $Fe(CO)_4B_7H_{12}^-$ which we find to be more stable than $B_7H_{12}^-$.

A new class of iron derivatives has been obtained from reactions of $Fe(CO)_5$ with B_5H_9 in a hot-cold reactor. With the hot surface at about 200° and the cold surface at around 20° , $Fe(CO)_3B_4H_8$ was obtained by Greenwood, Savory, Grimes, Sneddon, Davison, and Wreford (27). This compound is a square pyramid (Fig. 13).

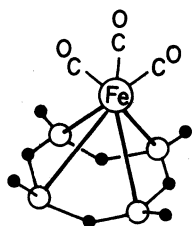


Fig. 13. The structure of $Fe(CO)_3B_4H_8$.

According to electron counting rules for skeletal electrons, the $Fe(CO)_3$ group furnishes 2 skeletal electrons and is therefore effectively isoelectronic with B-H (28). The $Fe(CO)_3-B_4H_8$ molecule is thus considered to be an isoelectronic analog of B_5H_9 and the earlier reported isomers of composition $(\pi-C_5H_5)CoB_4H_8$ (29). Interestingly, these compounds are also isoelectronic with $(\pi-C_4H_4)Fe(CO)_3$.

By frequently removing the evolved CO from the hot-cold reactor, Fehlner, Ullman, Ragaini, Mangion, and Shore (30) obtained $B_5H_9Fe(CO)_3$. This compound is the precursor to $B_4H_8Fe(CO)_3$ and can be considered to be the formal analog of B_6H_{10} . Based upon nmr spectra (1H , ^{11}B , ^{13}C) and an X-ray study of $B_5H_9Fe(CO)_3^-$ (30), $B_5H_9Fe(CO)_3$ is assigned a pentagonal pyramidal structure with the $Fe(CO)_3$ group occupying a basal vertex site (Fig. 14).

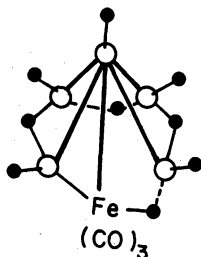
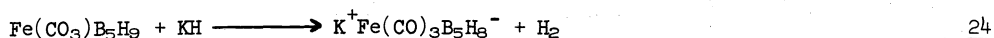


Fig. 14. The structure of $B_5H_9Fe(CO)_3$.

This molecule is nonrigid on the nmr time scale. The H associated with iron moves between the two possible bridging sites either through rotation or pseudo rotation of the $Fe(CO)_3H$ group. There is some nmr evidence for interaction of the H on Fe with the adjacent boron atom. If the H on Fe is involved in a β -center Fe-H-B bond, the breaking of this bond occurs as Fe-HB rather than the commonly observed M-H-B bond breaking which occurs in other fluxional metalloboranes (31). Thus H on Fe might be termed a pseudo terminal hydrogen since it appears always to be associated with the iron throughout the dynamic process. Interestingly, although the molecule appears to have an Fe-H-B bridge based on nmr spectra, valence

level photoelectron spectra correlate well with a structure with a terminal H on Fe (32).

The compound $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_9$ is a stronger Brønsted acid than B_6H_{10} ; it is readily deprotonated



(30). A point of special interest about this reaction is that a bridging H is removed from a B-H-B bond. Proton nmr spectra clearly reveal the presence of the H associated with Fe and also show that there are only two B-H-B bridges in the anion. With the exception of the difference in the number of B-H-B proton resonances, the nmr spectra of $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_9$ and $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_8^-$ are similar in appearance. In an X-ray structure determination of $\text{N}(\underline{n}\text{-C}_4\text{H}_9)_4^+$ $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_8^-$ all of the atoms in the anion were located (30), (Fig. 15).

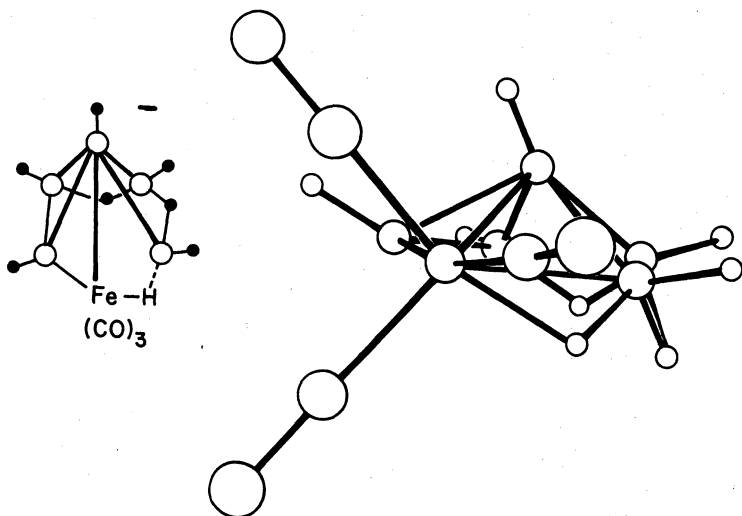
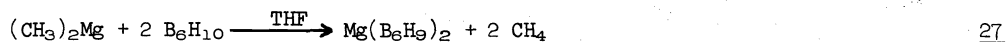
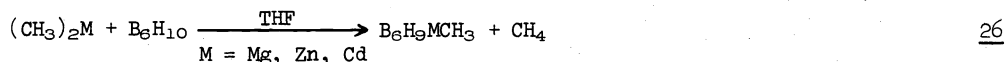
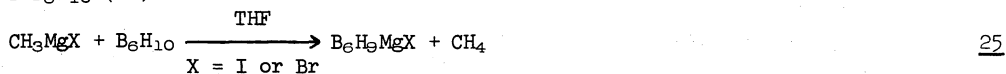


Fig. 15. The structure of $\text{Fe}(\text{CO})_3\text{B}_5\text{H}_8^-$

GROUP II METAL DERIVATIVES OF B_6H_{10}

Another type of metalloborane which we have prepared and studied has been formed from reactions of Grignard reagents and metal alkyls with B_6H_{10} by taking advantage of the inherent acidity of B_6H_{10} (11).



Variable temperature nmr spectra in methylene chloride solutions establish that these compounds are stereochemically nonrigid on the nmr time scale. From detailed studies involving variable temperature nmr spectra of $\text{Mg}(\text{THF-d}_8)_2(\text{B}_6\text{H}_9)_2$, it was established that bridging hydrogens and the metal are involved in the dynamic processes. The magnesium is probably involved in a dissociative exchange process whereas the bridging hydrogens are exchanging intramolecularly. At -100° , the nmr spectra provide evidence for metal insertion into a basal boron-boron bond on the anion. An X-ray study established the structure of $\text{Mg}(\text{THF})_2(\text{B}_6\text{H}_9)_2$ (11) (Fig. 16). The structural parameters are consistent with coordination of Mg to the B_6H_9 framework through insertion into the basal B-B bond. A point of further interest is that the B-B bond in the B_6H_9 group is not adjacent to the B-B bond in which the Mg is inserted. This is consistent with the structure of $\text{Fe}(\text{CO})_4\text{-B}_7\text{H}_{12}^-$ (Fig. 12) in which the inserted BH_3 and $\text{Fe}(\text{CO})_4$ groups are at non-adjacent sites.

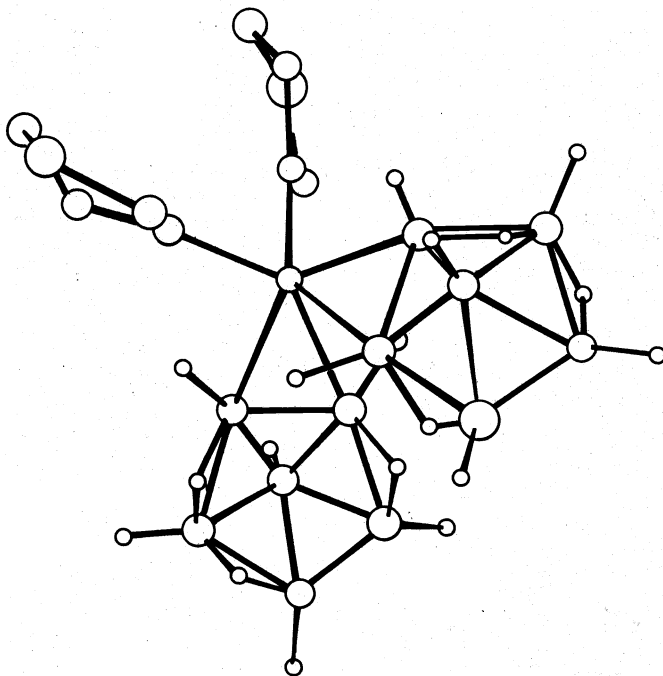


Fig. 16. The structure of $\text{Mg}(\text{THF})_2(\text{B}_5\text{H}_9)_2$.

DERIVATIVES OF THE HYPHO CLASS OF CLUSTER $(2n+8)$ SKELETAL ELECTRON SYSTEMS

In an earlier section of this paper the preparation of $\text{B}_5\text{H}_{12}^-$ was noted. This ion is the only binary hydride species prepared which appears to be a member of a newly recognized class of boranes which contain $2n+8$ skeletal electrons where n = the number of boron or vertex atoms (3a). This system is an extension of the commonly recognized classes of clusters: closo $2n+2$, nido $2n+4$, arachno $2n+6$ (28).

While explicit rules are available for counting skeletal electrons, for the present discussion it is sufficient to recognize that the number of skeletal electrons is implied in the formula of a neutral boron hydride if its structure consists of a single polyhedral fragment. Thus, for example, nido boron hydrides have the general formula B_nH_{n+4} and they contain $2n+4$ skeletal electrons. The ion $\text{B}_5\text{H}_{12}^-$ is the conjugate base of the hypothetical hydride B_5H_{13} , which is a B_nH_{n+8} hydride.

As noted earlier, the anion $\text{B}_5\text{H}_{12}^-$ is a highly fluxional species on the nmr time scale. On the basis of its nmr spectra its structure is believed to be a shallow four-sided pyramid (Fig. 4). It has been pointed out that as the number of skeletal electrons increases for a given number of vertices, the structure should become flatter and more open (28b, 28c). Thus, we expect $\text{B}_5\text{H}_{12}^-$ to be a more open structure than B_5H_9 and B_5H_{11} , the respective nido and arachno pentaboranes.

The nature of products of reactions of Lewis bases with boranes has been a subject of investigation ever since the first boron hydrides were prepared. The systems can be complex and the products can be markedly dependent upon a variety of factors (33). Most of the reactions studied to date have yielded fragments (cleavage products) of the boranes. As part of our general interest in the boron hydrides, we have been concerned with the possibility of preparing discrete, molecular adducts of molecular Lewis bases with boron hydrides. For example, we have been examining the adducts $\text{B}_5\text{H}_9\text{L}_2$ and $\text{B}_6\text{H}_{10}\text{L}_2$ where L = Lewis base. In principle, each ligand adds a pair of skeletal electrons to the boron framework. Thus, these adducts become hypho derivatives in that they can have $2n+8$ skeletal electrons. Such compounds are of interest since they represent extensions of the concept of classification of cluster systems. Furthermore, the compounds are of interest in their own right on the basis of sites of attachment of ligands and the possible fluxional character of these systems. Described below are some of the systems we have studied.

$\text{B}_5\text{H}_9\text{L}_2$

Bis-ligand adducts of B_5H_9 are analogs of the hypothetical $\text{B}_5\text{H}_{11}^{2-}$ dianion (H^- replaces L)

which is the conjugate base of $B_5H_{12}^-$ and the conjugate dibasic derivative of the hypothetical B_5H_{13} . We have examined $B_5H_9[P(CH_3)_3]_2$ (32, 34), $B_5H_9[N(CH_3)_3]_2$ (32, 34), and $B_5H_9-[N(CH_3)_2C_2H_4N(CH_3)_2]$ (34).

The structure of $B_5H_9[P(CH_3)_3]_2$ was determined (Fig. 17) from a single crystal X-ray study

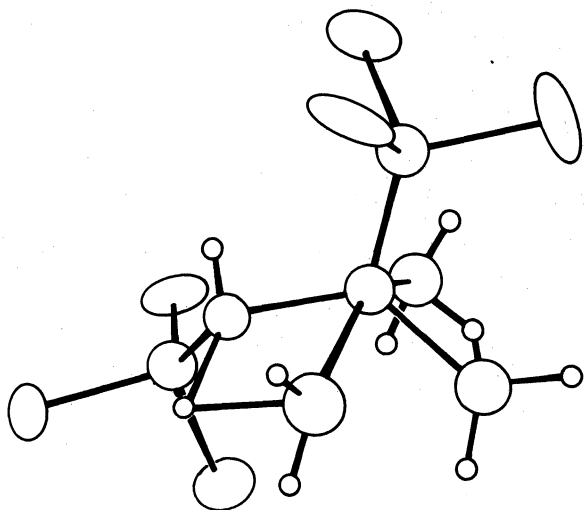


Fig. 17. The structure of $B_5H_9[P(CH_3)_3]_2$

(32) and found to differ from another suggested structure (35). This structure is a more open pyramid than the *nido* and *arachno* pentaboranes, B_5H_9 and B_5H_{11} . On the basis of this structure we might expect the isoelectronic analog $B_5H_{11}^{2-}$ to have a similar structure which differs from its conjugate acid $B_5H_{12}^-$ (Fig. 4) by having only a single H atom associated with the vertex boron.

Points of attachment of ligands in the $B_5H_9L_2$ adducts are dependent upon the ligand. Thus nmr spectra reveal attachment of $N(CH_3)_3$ groups at basal sites giving *cis* or *trans* isomers in the case of $B_5H_9[N(CH_3)_3]_2$ (Fig. 18), (32, 34, 35). In the case of $B_5H_9[N(CH_3)_2C_2H_4N-$

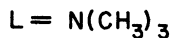
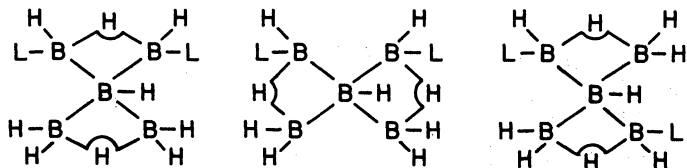


Fig. 18. Possible structures of $B_5H_9[N(CH_3)_3]_2$.

$(CH_3)_2]$ nmr spectra favor a chelate structure involving a single basal boron site (Fig. 19). However, basal apical attachment of the ligand cannot be ruled out unequivocally.

NMR spectra reveal that the $B_5H_9L_2$ adducts described above are stereochemically nonrigid with all of the hydrogens on the basal borons being involved in exchange averaging, while the boron atoms and ligands remain essentially fixed (32, 34).

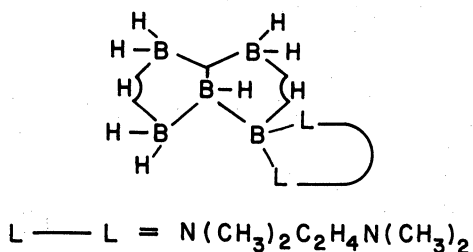


Fig. 19. Suggested structure of $B_5H_9[N(CH_3)_2C_2H_4N(CH_3)_2]_2$.

$B_6H_{10}L_2$

Bis-ligand adducts of B_6H_{10} are formal analogs of the hypothetical $B_6H_{12}^{2-}$ dianion (H^- replaces L) which are the conjugate dibasic derivatives of B_6H_{14} .

The structure of $B_6H_{10}[P(CH_3)_3]_2$ has been determined from a single crystal X-ray study (Fig. 20) (36).

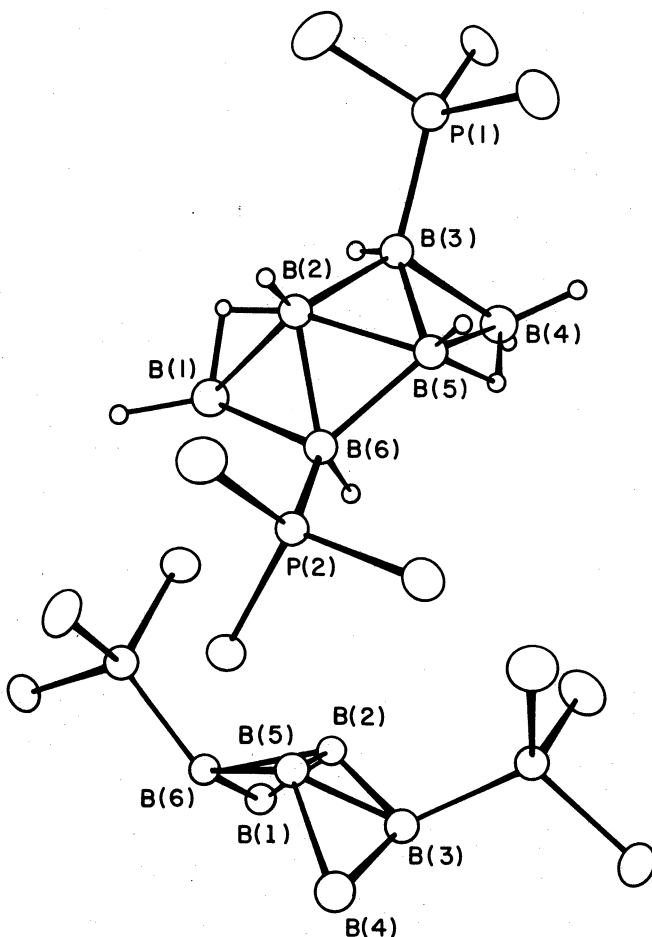


Fig. 20. a) The molecular structure of $B_6H_{10}[P(CH_3)_3]_2$. b) The conformation of B_6 framework in $B_6H_{10}[P(CH_3)_3]_2$.

In this case, the effect of going from an arachno $2n + 6$ system to a hypho $2n + 8$ system is more marked than in the $B_5H_9L_2$ example. The structure of $B_6H_{10}[P(CH_3)_3]_2$ is an open, flat arrangement. The relationship of this structure to that of a pentagonal pyramidal arrangement in B_6H_{10} , can be visualized by placing B(1) between B(4) and B(6) to form a pentagonal plane.

The ^{11}B decoupled proton nmr spectra reveal that this compound is fluxional on the proton nmr time scale, but only bridging hydrogens and hydrogens on borons 1 and 5 seem to be involved in the dynamic process (36).

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